LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

**M.Sc.** DEGREE EXAMINATION - **CHEMISTRY**

FIRST SEMESTER – NOVEMBER 2010

# CH 1808 - QUANTUM CHEMISTRY & GROUP THEORY

Date : 03-11-10 Dept. No. Max. : 100 Marks

Time : 1:00 - 4:00

## Part-A

**ANSWER ALL QUESTIONS (10 × 2 = 20)**

1. Give the Laplacian operator in spherical polar coordinates. What are their limits of integration?
2. Show the wave function Ae-2x is an eigen function of the operator d2/dx2. What is the eigen value?
3. The energy of a particle moving in a cubic box of side ‘a’ is 3h2/2ma2. What is its degeneracy?
4. CO absorbs energy in the microwave region of the spectrum at 1.93 x 1012 Hz. This is attributed to the J=0 to J=1 transition. Calculate the moment of inertia of the molecule.
5. What is the value of [**y,py**]? What is its physical significance?
6. Simple Harmonic Oscillator has zero as one of the quantum numbers while the particle in a box model does not have. Why?
7. What is a boson? Give an example.
8. Write the Hamiltonian operator for the H2+ molecule in atomic units defining each term involved in it.
9. Prove that the operations *S2* and *i* have the same effect.
10. Predict the trace of C3 operation.

### Part-B

**ANSWER ANY EIGHT QUESTIONS (8 × 5 = 40)**

1. What is a hermitian operator? Show that the wave functions corresponding to two different eigen values of a Hermitian operator are orthogonal.
2. State the variation theorem. Apply it to the problem of particle in a 1-D box of length a, by taking ψ = x(a-x) as a trial function for 0≤x≤a.
3. Write the Schrödinger equation for 1-D harmonic oscillator. Verify ψ = (2a/π)1/4exp(-ax2) is an eigen function of the Hamiltonian operator for the 1-D harmonic oscillator.
4. The force constant of 79Br-79Br is 240 Nm-1. Calculate the fundamental vibrational frequency and the zero-point energy of the molecule.
5. What is a Slater determinant? Write the four Slater determinants for the excited state of He atom (1s, 2s).
6. Explain briefly with a suitable example:

(a) Bohr’s Correspondence Principle (b) Born-Oppenheimer Approximation.

1. The wave function of 1s orbital of Li2+ is Ψ1s = (1/√π) (Z/a0)3/2 exp(-Zr/a0), where a0 is the most probable distance of the electron from the nucleus. Show that the average distance is a0/2. [Help: 0∫∞ xne-qx = n!/qn+1]
2. Write the Hamiltonian in atomic units and explain briefly how the Valance Bond (Heitler-London) treatment of H2 molecule makes up for what MO theory lacks.
3. Explain the following with a suitable example:
4. Spherical Harmonics (b) Quantum mechanical tunneling. (2+3)
5. What is a term symbol? Explain the origin of the fine structure of the emission spectrum of sodium vapor used in street lighting using term symbols.
6. List down the symmetry elements and symmetry operations of trans-1,3-dibromo cyclobutane and Furan.
7. Identify T1, T2, X and Y of the following partially constructed character table.

|  |  |  |
| --- | --- | --- |
| X | E | i |
| T1 | 1 | 1 |
| T2 | 1 | Y |

### Part-C

**ANSWER ANY FOUR QUESTIONS (4 × 10 = 40)**

1. a) Derive the wave function and energy for the particle in a 1-D box.

b) For butadiene CH2=CH-CH=CH2, take the box length as 7.0Å and use the particle in 1-D box as model to estimate theoretically the wavelength of light absorbed when a pi electron is excited from the highest-occupied to the lowest vacant box level. If the experimental value is 2170Å, comment on your theoretical model. (7+3)

24. (a) Derive the time-independent Schroedinger equation from the time-dependent and prove that the

property such as electron density is time independent although the wave function describing an

electron is time dependent

b) The microwave spectrum of the CN radical shows a series of lines spaced by a nearly constant

amount of 3.798 cm-1. What is the bond length of CN? (6+4)

1. a) What are the three approximations Hückel employs in defining the integrals of the secular

determinant in the case of π electrons?

b) Write down the secular determinant by applying Huckel's method to the allyl cation and obtain the

expressions for the energy levels of the π electrons. (3+7)

1. (a) In solving the H2+ problem using the LCAO method, the lowest energy obtained is given

by E+ = (HAA + HAB) / (1+SAB) where A and B refer to the two hydrogen nuclei. Explain each of the integrals in the above equation and their significance.

1. Show that the wave function describing the 1s orbital of H-atom is normalized,

given: Ψ1s = (1/√π) (Z/a0)3/2 exp(-Zr/a0). [Useful integral: 0∝∫xne-axdx = n!/an+1]

(6+4)

27. What is a permutation operator? State and illustrate the Pauli Exclusion Principle for the ground state of

He atom that wave functions must be antisymmetric in the interchange of any two electrons.

28. Work out the hybridization for sigma bonding by Boron in BCl3 molecule using the

following character table.

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| --- |
|  |

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **E** | **2C3** | **3C'2** | **σh** | **2S3** | **3σv** |  |  |
| **A'1** | 1 | 1 | 1 | 1 | 1 | 1 |  | x2+y2, z2 |
| **A'2** | 1 | 1 | -1 | 1 | 1 | -1 | Rz |  |
| **E'** | 2 | -1 | 0 | 2 | -1 | 0 | (x, y) | (x2-y2, xy) |
| **A''1** | 1 | 1 | 1 | -1 | -1 | -1 |  |  |
| **A''2** | 1 | 1 | -1 | -1 | -1 | 1 | z |  |
| **E''** | 2 | -1 | 0 | -2 | 1 | 0 | (Rx, Ry) | (xz, yz |

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